

1,060,102



PATENT SPECIFICATION

NO DRAWINGS

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Int. Cl.:—D 06 m // C 08 f

COMPLETE SPECIFICATION

Treatment of Textile Fibres

We, J. R. GEIGY A.G., a Swiss Company of Schwarzwaldallee 215, Basle 21, Switzerland, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to and has among its objects the provision of novel processes for treating hydrogen donor textile materials and the products of such processes. A broad object of the invention concerns modification of hydrogen donor textile fibers by treating them with copolymers derived from acryloyl or methacryloyl chloride. A special object of the invention is the provision of such treatments involving the use of copolymers of (a) acryloyl or methacryloyl chloride and (b) fluoroalkyl acrylates or methacrylates, applied to and reacted with the textile material to provide such benefits as improved shrinkage resistance and enhanced repellency toward oil and water. Further objects and advantages of the invention will be evident from the following description wherein parts and percentages are by weight unless otherwise specified.

In the processing of textiles it is often desirable to modify the inherent properties of the fibers, for example, to improve their shrinkage characteristics. Various procedures have been advocated for such purposes and they usually involve treatment of the textile with a resinous material. A common fault of many of these procedures is that the modification has but a temporary effect as the material is removed from the fibers when they are subjected to laundering or dry cleaning.

40 In accordance with the invention, textile [Price 4s. 6d.]

materials are treated with certain copolymers which react with the textile materials so that the modification achieved is deep-seated and durable. In other words, the invention yields the advantage that the copolymer applied to the fibers is not just a physical coating but is chemically bonded or grafted to the fibers.

According to the present invention there is provided a process of treating a hydrogen-donor textile material to improve its properties which comprises reacting said textile material with a copolymer applied thereto as such or formed in situ on the textile material, said copolymer being a copolymer of (1) an acid chloride which is acryloyl chloride or methacryloyl chloride and (2) a different compound which is copolymerisable with said acid chloride, which contains at least one $\text{CH}_2=\text{C}<$ grouping and which is free from any hydrogen atom reactive with an acid chloride grouping.

Such copolymers contain pendant acid

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chloride ($-\text{C}(\text{Cl})$) groups which react with those radicals of the textile material which have active hydrogen atoms. Such radicals may also be termed hydrogen-donor radicals and include groups such as hydroxyl, primary or secondary amine, primary amide, thiol and carboxyl groups. Typically, with cellulosic textile it is believed that the copolymers are chemically bound to the textile through ester linkages formed by reaction of hydroxyl groups on the textile with the pendant acid chloride groups of the copolymer. With protein fibers such as wool, the copolymers are believed to be chemically bound to the textile through any one or more of such linking radicals as: ester groups (by reaction of the pendant

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acid chloride groups of the copolymer with hydroxyl groups on the wool): amide groups (by reaction of the pendant acid chloride groups of the copolymer with primary or 5 secondary amine groups on the wool): imide groups (by reaction of the pendant acid chloride groups of the copolymer with primary amide groups on the wool): and thioester groups (by reaction of the pendant 10 acid chloride groups of the copolymer with thiol groups of the wool). The fact that a chemical bonding is achieved rather than a mere physical adhesion has been demonstrated by experiments wherein it was attempted to 15 dissolve the grafted copolymer with solvents which are capable of dissolving the copolymers in bulk — see Examples I (Part D) and III, below. It was found that no substantial removal of copolymer was obtained, 20 thus demonstrating a chemical bonding of the copolymers to the fibers.

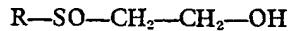
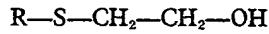
PREPARATION OF THE COPOLYMERS

Examples of monomeric substances which 25 may be copolymerised with acryloyl or methacryloyl chloride to produce copolymers for use in practicing the invention are set forth below by way of illustration but not limitation:

30 Alkyl esters of acrylic acid and alkyl esters of any of the various α -alkylacrylic or α -haloacrylic acids, e.g. the methyl, ethyl, propyl, isopropyl, butyl, amyl, hexyl, octyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, cyclohexyl and oleyl esters of acrylic, 35 methacrylic, ethacrylic, propacrylic, chloroacrylic and bromoacrylic acids.

Alkyl acrylates or methacrylates containing 40 an oxygen bridge, typically methoxyethyl acrylate, ethoxyethyl acrylate, propoxyethyl acrylate, butoxyethyl acrylate, octoxyethyl acrylate, cyclohexoxyethyl acrylate, benzoxyethyl acrylate, phenoxyethyl acrylate, methoxyethyl methacrylate and phenoxyethyl methacrylate.

45 Acrylates containing such radicals as thioether, sulphone, or sulphoxide, for example, the esters of acrylic acid or methacrylic acid with alcohols of the types:



wherein R is an alkyl radical such as methyl, 55 ethyl, propyl or butyl, or an aryl or aralkyl radical such as phenyl, tolyl, benzyl or phenylethyl.

Vinyl esters of fatty acids, e.g. vinyl acetate, 60 propionate, butyrate, valerate, caprylate, caprate, laurate, myristate, palmitate, stearate and oleate.

Allyl and methallyl esters of fatty acids,

e.g. allyl and methallyl acetates, propionates, butyrates, valerates, caprylates, caprates, laurates, myristates, palmitates, stearates and oleates.

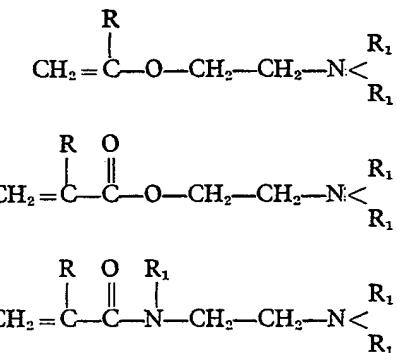
N - Dialkyl acrylamides and N - dialkyl α -substituted acrylamides, for example, N - dimethyl, N - diethyl, N - dipropyl, N - dibutyl, N - diamyl, N - dihexyl, N - dioctyl and N - didodecyl acrylamides, methacrylamides, ethacrylamides and propacrylamides. 70

Hydrocarbons and halogenated hydrocarbons such as styrene, α - methylstyrene, dimethylstyrenes, vinyl naphthalenes, dichlorostyrenes, vinyl chloride, vinyl bromide, vinylidene chloride and vinylidene bromide. 75

Ketones such as methyl vinyl ketone, ethyl vinyl ketone, isopropyl vinyl ketone and other alkyl vinyl ketones, methyl isopropenyl ketone and methyl allyl ketone.

Itaconic diesters, for example, the dimethyl, diethyl, diisopropyl, dibutyl, dihexyl, didodecyl and other dialkyl esters of itaconic acid. Diaryl and diaralkyl esters of itaconic acid, e.g. diphenyl itaconate, dibenzyl itaconate and di - (phenylethyl) itaconate. 80

Other compounds containing the typical $CH_2=C<$ grouping such as cyanostyrenes, vinyl thiophene, vinyl pyridine, vinyl pyrrole, acrylonitrile, methacrylonitrile and alkyl vinyl sulphones such as ethyl vinyl sulphone. Compounds of the types: 85

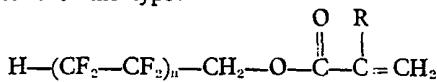


where R is H or CH_3 and wherein R_1 is a lower alkyl group such as CH_3 or C_2H_5 . 95

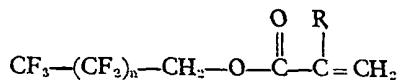
Although it is generally preferred to copolymerise the acryloyl or methacryloyl chloride with an individual monomer such as those exemplified above, it is within the purview 100 of the invention to use mixtures of two or more monomers. Indeed, it is helpful in some instances to use a highly polymerisable compound such as acrylonitrile in conjunction with a monomer of lesser activity such 105 as vinyl acetate, to promote conjoint copolymerization with the acryloyl (or methacryloyl) chloride.

In a particularly preferred modification of 110 the invention, textiles, especially wool textiles, are treated with copolymers of (1) acryloyl or methacryloyl chloride and (2)

fluoroalkyl esters of acrylic or methacrylic acid, that is, alkyl esters of acrylic or methacrylic acids wherein at least one hydrogen atom of the alkyl radical is replaced by fluorine. By using such fluorinated copolymers one achieves in a single procedure a plurality of useful effects, namely, increase in the resistance of the wool to shrinking and felting when it is laundered, an enhanced resistance to becoming soiled, enhanced water repellency and oil repellency, and even increased resistance to such wool-degrading agents as acids, alkalis, and aqueous oxidising media. It is also to be noted that such a multi-purpose effect is attained with only a minor proportion of the fluorinated copolymer chemically bonded to the wool, that is, from 0.5 to 5%, based on the weight of the textile, and there is no significant loss of the hand of the wool. Typical of the fluoroalkyl esters which may be copolymerised with acryloyl or methacryloyl chloride to produce copolymers for use in this modification of the invention are: perfluoro-*t*-butyl acrylate, perfluoro-*t*-butyl methacrylate, and esters of the type:



wherein R is H or CH₃ and n is an integer from 2 to 6. Typical examples of this type of primary perfluoroalkyl ester are: 1,1,5-trihydroperfluoropentyl acrylate and methacrylate, 1,1,7-trihydroperfluoroheptyl acrylate and methacrylate, 1,1,9-trihydroperfluorononyl acrylate and methacrylate, 1,1,11-trihydroperfluoroundecyl acrylate and methacrylate and 1,1,13-trihydroperfluorotridecyl acrylate and methacrylate. Usually, it is preferred that the fluoroalkyl radical contain at least 3 fluorine atoms and an especially desirable type of fluoroalkyl ester for the multi-purpose treatment mentioned above is one wherein the fluoroalkyl radical not only contains at least 3 fluorine atoms but also has its omega carbon atom completely fluorinated. Typical of these particularly preferred fluoroalkyl esters are those of the type:



wherein R is H or CH₃ and n is an integer of from 0 to 18. Illustrative examples of such compounds are the acrylic and methacrylic acid esters of: 1,1-dihydroperfluoropropyl alcohol, 1,1-dihydroperfluorobutyl alcohol, 1,1-dihydroperfluorohexyl alcohol, 1,1-dihydroperfluoroctyl alcohol, 1,1-dihydroperfluorodecyl alcohol, 1,1-dihydroperfluorododecyl alcohol, 1,1-dihydroperfluorohexadecyl alcohol and 1,1-dihydroperfluoroctadecyl alcohol. In a variation of this

modification of the invention, one uses a polymer prepared by copolymerizing (1) acryloyl or methacryloyl chloride with (2) a mixture of a fluoroalkyl ester of acrylic or methacrylic acid and a non-fluorinated alkyl (at least C₈) acrylate or methacrylate. Typical polymers in this category are those derived from methacryloyl chloride, 1,1-dihydroperfluoroctyl acrylate, and an alkyl methacrylate such as lauryl, myristyl, palmityl, or stearyl methacrylate. Another method involves use of a mixture of copolymers, i.e. applying to the wool a mixture of two different copolymers, one being, for example, a copolymer of acryloyl (or methacryloyl) chloride and a fluoroalkyl acrylate or fluoroalkyl methacrylate, the other being, for example, a copolymer of acryloyl (or methacryloyl) chloride and a non-fluorinated alkyl (at least C₈) acrylate or methacrylate. Specifically, such a mixture may comprise, as an illustrative example, (1) a copolymer of methacryloyl chloride and 1,1-dihydroperfluoroctyl acrylate and (2) a copolymer of methacryloyl chloride and lauryl or stearyl methacrylate.

The copolymers used in practising the invention are prepared by conventional polymerisation techniques. These essentially involve intimate contact under anhydrous conditions of the acryloyl (or methacryloyl) chloride with the other monomer to be copolymerised therewith. The reactants may be copolymerised under the influence of heat, light, or heat plus light in the presence or absence of a polymerisation catalyst such as, benzoyl peroxide, acetyl peroxide, lauroyl peroxide, di-*tert*-butyl peroxide, or other organic peroxide or other catalyst which is free from a hydrogen atom or atoms that would react with the acid chloride grouping. The copolymerisation is continued until there is formed a viscous liquid to solid material which is soluble in common solvents for resins, typically toluene, xylene, benzotrifluoride, ethyl acetate and 1,3-bis-(trifluoromethyl)benzene. Ultraviolet light is more effective than ordinary light in catalyzing the polymerisation. The polymerisation may be conducted in the bulk or in the solution state, for instance, in solution in an inert solvent such as benzene, toluene, xylene, dioxane, dibutyl ether, butyl acetate, chlorobenzene, ethylene dichloride, methyl ethyl ketone, or fluorohydrocarbons such as benzotrifluoride or 1,3-bis-(trifluoromethyl)benzene. The temperature of polymerisation may be varied as desired or the conditions may require and generally will be within the range from 20° to 150°C when polymerisation is effected in the absence of a solvent. When polymerisation is carried out in solution, it is generally carried out at the boiling temperature of the solution. It is obvious that in any particular case, the temperature of

polymerisation should be below the decomposition temperature of the monomers being reacted and that of the copolymer being prepared. In a preferred modification of the process, the monomers are reacted in bulk, i.e. with no solvent and copolymerisation is effected at a temperature of about 70—100°C with the use of an α,α' -azodialkylcyanide type catalyst, such as α,α' -azadiisobutyronitrile or α,α' -azobis-(α,γ -dimethylvaleronitrile).

In preparing the copolymers of the invention, the proportions of acryloyl chloride (or methacryloyl chloride) and the other monomer may be varied widely. In general, one copolymerises 10 to 90% of acryloyl or methacryloyl chloride and 90 to 10% of the other monomer. In many instances, for example, in preparing the preferred fluorinated copolymers, one uses one mole of acryloyl or methacryloyl chloride in conjunction with 1 to 10 moles of the other monomer, e.g. the fluoroalkyl acrylate or methacrylate.

APPLICATION OF THE COPOLYMER TO THE TEXTILE

The copolymers of the invention may be applied to the textile in various ways. One technique involves applying the copolymer as such to the textile, using heating to make the copolymer flow and distributing it with calender rolls. Generally, this technique is not a preferred one because it causes a stiffening of the textile and is thus suitable only in instances where such stiffening effect is desirable or tolerable. A preferred technique involves dissolving the copolymer in an inert, volatile solvent and applying the resulting solution to the textile material. Typical of the solvents which may be used are benzene, toluene, xylene, dioxane, diisopropyl ether, dibutyl ether, butyl acetate, chlorinated hydrocarbons such as chloroform, carbon tetrachloride, ethylene dichloride, trichloroethylene, 1,3-dichlorobenzene, fluorohydrocarbons such as benzotrifluoride and 1,3-bis-(trifluoromethyl)benzene, and petroleum distillates such as petroleum naphthas. The concentration of the copolymer in the solution is not critical and may be varied depending on such circumstances as the solubility of the copolymer in the selected solvent, the amount of copolymer to be deposited on the fibers and the viscosity of the solution. In general, a practical range of concentration would be from 1% to 25%. The solution may be distributed on the textile material by any of the usual methods, for example, by spraying, brushing, padding or dipping. A preferred technique involves immersing the textile in the solution and then passing it through squeeze rolls to remove the excess of liquid. Such techniques as blowing air through the treated textile may be employed to reduce the amount of liquid

which exists in interstices between fibrous elements. In any case, the conditions of application are so adjusted that the textile material contains the proportion of copolymer desired. Usually, the amount of copolymer is from 0.5 to 20%, based on the weight of the textile material but it is obvious that higher proportions of copolymer may be used for special purposes. Usually, in treating textiles such as fabrics the amount of copolymer is limited to a range of 0.5 to 10% to attain the desired end such as shrink resistance without interference with the hand of the textile.

In another technique a pre-formed copolymer is not used but the textile material is impregnated with a solution containing the acryloyl chloride (or methacryloyl chloride) plus the other monomer copolymerisable therewith. The solvent for forming the solution is an inert, volatile, organic solvent as typified by those listed above. In this technique the copolymerizable monomers react during the curing step (described below), forming the copolymer *in situ* and chemically bonding the so-formed copolymer to the textile fibres. To assist the *in situ* polymerization, the solution of the unreacted polymers may contain a minor proportion of a suitable polymerization catalyst or the catalyst may be applied in a separate step before or after the monomers are deposited on the fibrous material. A typical embodiment of this system may take the following form: A solution, in ethyl acetate, is prepared containing equimolar proportions of methacryloyl chloride and ethyl acrylate. The textile material is immersed in this solution, then passed through squeeze rolls to press out excess solution and leave about 1 to 5% of the monomers, based on the weight of the textile. The treated textile is then passed through a dilute solution of benzoyl peroxide in an inert, volatile solvent or exposed to ultraviolet light. The treated textile is then cured as described below. It is obvious that many variations may be applied in this system; for example, the copolymerizable monomers may be applied in separate solutions in inert, volatile solvents and the catalyst may be incorporated in one of these solutions or applied in a separate step.

After application of the copolymer (or the reactive monomers) the treated textile is cured (heated) to effect reaction between the textile material and the copolymer, or to effect formation of the copolymer from the reactive monomers, and to bond the so-formed polymer to the fibres. In cases where the polymer is applied as a dispersion, that is, a solution, emulsion, or suspension, the solvent or other volatile dispersing medium is preferably evaporated prior to the curing operation. Such prior evaporation is not a critical step and the evaporation may be

simply effected as part of the curing step. The temperature applied in the curing step is not critical and usually is within the range from 50°C to 150°C. It is obvious that the time required for the curing will vary with such factors as the reactivity of the selected copolymer, the type of textile material, and particularly the temperature so that a lower curing temperature will require a longer curing time and vice versa. It will be further obvious to those skilled in the art that in any particular case the temperature of curing should not be so high as to cause degradation of the textile or the copolymer.

15 In many cases an adequate cure is effected by heating the treated textile in an oven at 100°C for 5 to 60 minutes.

Instead of employing the above described technique of application of the copolymer followed by curing, the application and curing can be done in a single step. In this technique the copolymer is formed into a solution of an inert, volatile, organic solvent such as those listed above, the textile material

20 is entered into the solution, and the system heated, for example, to 100°C or up to reflux temperature (boiling point) of the selected solvent. In this way the copolymer reacts directly with the textile material.

25 Usually to promote the reaction, there is added to the solution a minor proportion (i.e., 1 to 10% of the weight of the copolymer) of pyridine, dimethyl-aniline, of other tertiary amine free from reactive hydrogen atoms to act as an HCl-acceptor. Reaction-promoting agents such as dimethylformamide or diethylformamide may be used in conjunction or in place of the tertiary amine.

30 Another method for applying the copolymer is one which utilizes the technique of forming condensation polymers (e.g., polyamides) *in situ* on textiles by interfacial polymerization as described in Specification No. 913,370. Basically the method involves forming, under

35 interfacial polymerization conditions, an organic condensation polymer *in situ* on the fibres of the textiles while providing the copolymer (i.e., a copolymer derived from acryloyl chloride or methacryloyl chloride, as

40 described hereinabove) at the locus where the interfacial polymerization takes place. As a result of such procedure, the copolymer is chemically bonded to the textile fibres, directly, or through chemical union with the

45 condensation polymer as it is being formed on the fibres. Moreover, such chemical bonding may involve both (a) reaction of the copolymer with the textile fibres, plus (b) reaction of the copolymer with the condensation polymer as the latter is being formed. In a typical embodiment of this system, the textile is first impregnated with an aqueous solution of hexamethylene di-

50 amine. Then, the textile is impregnated with a solution containing sebacoyl chloride and a selected copolymer (for example, a copolymer, of methacryloyl chloride and 1,1-dihydroperfluorobutyl acrylate) dissolved in a water-immiscible solvent such as toluene. By such treatment the textile fibres are coated with superposed layers of the mutually-immiscible solutions. Under those conditions the diamine and the sebacoyl chloride react almost instantaneously at the interface between the two phases, producing *in situ* on the fibres a high molecular weight, resinous polyamide which is chemically bonded to the fibres. The methacryloyl chloride-perfluorobutyl acrylate copolymer being present at the locus of this sphere of action enters into reaction directly with the fibres and/or the polyamide as it is formed and, in any event, is thus chemically bonded to the fibres. The plan exemplified above may be utilized in conjunction with formation, by interfacial polymerization, of any of the various types of condensation polymers disclosed in Specification No. 913,370, for example: Polyamides — by employing serial impregnation of the textile with (1) an aqueous solution of a diamine and (2) a solution of diacid chloride in a water-immiscible solvent; Polyurethanes — by employing serial impregnation of the textile with (1) an aqueous solution of a diamine and (2) a solution of a bis-chloroformate in a water-immiscible solvent; Polyureas — by employing serial impregnation of the textile with (1) an aqueous solution of a diol and (2) a solution of a diacid chloride in a water-immiscible solvent; Polyesters — by employing serial impregnation of the textile with (1) an aqueous solution of a diol and (2) a solution of a bis-chloroformate in a water-immiscible solvent; Polycarbonates — by employing serial impregnation of the textile in (1) an aqueous solution of a diol and (2) a solution of a bischloroformate in a water-immiscible solvent; Interpolymers — by employing serial impregnation of the textile in parts of solutions which contain complementary reagents that form interpolymers, for instance, (1) an aqueous solution of a diamine and (2) a solution containing both a diacid chloride and a diisocyanate in a water-immiscible solvent (to form a copolyamide-urea). In any of such applications, the copolymer in accordance with the invention is added to the solution designated "2" — that is, the one containing the water-immiscible solvent. The amount of copolymer added may be varied depending, for example, on the proportion of condensation polymer and copolymer desired to be applied to the textile. The condensation polymer-forming intermediates used in this system may be any of those listed in Specification No. 913,370 in the section entitled "Components A and B". Typical illustrative examples of these intermediates are: Diamines — ethylene diamine,

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trimethylene diamine, hexamethylene diamine, 1,4 - phenylene diamine, and 1,4 - diaminocyclohexane; Diols — ethylene glycol, diethylene glycol, octane - 1,8 - diol, cyclohexane - 1,4 - diol, hydroquinone, bis - (para-hydroxyphenyl)methane and 2,2 - bis - (para-hydroxyphenyl)propane. Diacid chlorides — succinyl chloride, adipyl chloride, sebacyl chloride, suberyl chloride, phthalyl chloride and hexahydrotetraphthalyl chlorides: Bis-chloroformates — ethylene glycol, diethylene glycol, hexamethylene glycol, hydroquinone and cyclohexane - 1,4 - diol bischloroformates: Diisocyanates — ethylene, butylene, hexamethylene, phenylene, tolylene, or bitolyene diisocyanates. When the copolymers of the invention are applied in conjunction with interfacial polymerization as described above, the treated textile may be cured as described hereinabove to ensure chemical bonding of the copolymer to the textile material.

Although the present invention is of particular advantage in its application to wool, this is by means the only type of fibre which comes into the ambit of the invention. Generically, the invention is applicable to the treatment of any hydrogen-donor textile material and this material may be in any physical form, e.g., bulk fibres, filaments, yarns, threads, silvers, roving, top, webbing, cord, tapes, woven or knitted fabrics, felts or other non-woven fabrics, garments or garment parts. Illustrative examples of hydrogen-donor textile materials are: polysaccharide-containing textiles, for instance, those formed of or containing cellulose or regenerated celluloses, e.g., cotton, linen, hemp, jute, rami, sisal, cellulose acetate rayons, cellulose acetate-butylate rayons, saponified cellulose acetate rayons, viscose rayons, cuprammonium rayons, ethyl cellulose, fibres prepared from amylose, algin, or pectins; mixtures of two or more of such polysaccharide-containing textiles; protein-containing textiles, for instance, those formed of or containing wool, silk, animal hair, mohair, regenerated protein fibres such as those prepared from casein, soybeans, peanut protein, zein, gluten, egg albumin, collagen, or keratins, such as feathers, animal hoof or horn; mixtures of any two or more of said protein-containing textiles; mixtures of polysaccharide-containing textiles and protein-containing textiles, e.g., blends of wool and cotton, wool and viscose, rayon; textiles formed of or containing synthetic resins having hydroxy groups in the molecule, e.g., alkyd resins containing hydroxyl groups, polyvinyl alcohol, and partially esterified or partially etherified polyvinyl alcohols; synthetic silk, e.g., nylon and polyurethanes; mixtures of nylon or other synthetic silk with a polysaccharide or protein fibre; mixtures of synthetic resins containing hydroxyl groups with nylon, polyurethanes, polysaccharide, or protein fibres. By applying the invention to

hydrogen-donor textiles, such as those exemplified above, desirable results are attained. These include: increasing the resistance of the textile to shrinking or felting when subjected to washing operations; increasing the resistance of the textile to becoming soiled in use; enhancing the oil- and water-repellency of the textile and decreasing the tendency of the textile to becoming creased or wrinkled during wear or during washing and drying operations. Moreover, these desirable effects are attained without impairing such desirable fibre characteristics or tensile strength, abrasion resistance, porosity, and the hand of the material so that the textiles modified in accordance with the invention may be used in fabricating garments or other conventional structures of any kind.

EXAMPLES

The invention is further demonstrated by the following illustrative examples.

The various tests referred to in the examples were carried out as follows:

Oil Repellency: The 3M oil repellency test described by Graeck and Paterson, Textile Research Journal, 32, pages 320—331. 1962. Ratings are from 0 to 150, with the higher values signifying the greater resistance to oil penetration.

Water Repellency: AATC spray test, method 22—1952. Ratings are from 0 to 100 with the higher values signifying greater resistance to water penetration.

Home Laundering Procedure: An agitator-type home washing machine was operated under the following conditions: Low water level (about 11 gal.); wash temperature, 115—125°F.; rinse temperature, 95—115°F.; normal agitation; 12-minute wash cycle; load—2 pounds ballast plus samples, total weight not exceeding 4 pounds; 100 cc "Tide" detergent. Washed samples were dried 15 minutes in a forced draft oven at 160°F.

Accelerator Shrinkage Test: The fabric samples (5" x 6") were milled at 1780 rpm for 2 minutes at 40°C in an Accelerator with 17 sodium oleate solution, using a liquor-to-fabric ratio of about 50 to 1. After this washing operation, the samples were measured to determine their area and the shrinkage calculated from the original area. The Accelerator is described in the American Dyestuff Reporter 45, p. 635, Sept. 10, 1956. The 2-minute wash in this device is equal to approximately 15 home launderings.

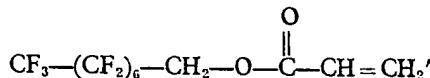
Abbreviations: In the following examples the compound 1,1-dihydroperfluorooctyl acrylate is referred to as PFOA; methacryloyl chloride is MAC; and copolymers of these compounds are referred to as poly-PFOA/MAC. A numerical ratio following the designation of the copolymer refers to a molar ratio of the monomers, for example, "poly-PFOA/MAC 3/1" means the copolymer pre-

pared from 3 moles PFOA and 1 mole of MAC.

EXAMPLE I

A: Preparation of PFOA/MAC Copolymers

5 *Poly-PFOA/MAC 3/1:* Into a dry, 4-oz. vial were placed 11.8 g. (0.026 mole) of 1,1-dihydroperfluoroctyl acrylate,



10 0.92 g. (0.0088 mole) of methacryloyl chloride, and 50 mg. of α,α' - azodiisobutyronitrile. The vial was closed with a screw cap and placed in a 78°C bath for 3-4 hours. The copolymer was a tacky solid with an inherent viscosity of 0.21 at 25°C in 1,3 - bis - (trifluoromethyl)benzene.

15 *Poly-PFOA/MAC 1/1 and Poly-PFOA/MAC 9/1* were prepared in the same manner as above but substituting the appropriate molar proportions of PFOA and MAC, namely, equimolar proportions of PFOA and MAC for the 1/1 copolymer and 9 moles of PFOA to 1 mole of MAC for the 9/1 copolymer. Both the 1/1 and 9/1 copolymers were tacky solid resins.

20 B: Application of PFOA/MAC Copolymers

25 Each of the PFOA/MAC copolymers described in Part A was dissolved in a minimum quantity of benzotrifluoride, then the solution was diluted with the same solvent to the desired concentration. In this way,

solutions at concentration levels of 1.5%, 3% and 7% were prepared from each of the copolymers. (The different concentration levels were used to enable application of varying amounts of the copolymers onto a fabric). The solutions were applied to samples of wool fabric (7.06 oz/sq.yd. undyed woollen flannel, 33 ends and 33 picks per inch) in the following manner:

30 The fabric was immersed in the copolymer solution, then passed through squeeze rolls to provide a wet pick-up of about 70%. The treated fabric was then placed in an oven at 105°C for about 1.5 hours in order to cure the resin and bond it to the wool. After curing, the samples were weighed to determine the amount of copolymer on the fabric.

C: Oil and Water Repellency and Shrinkage Test of PFOA/MAC-Treated Fabric

35 The treated fabric samples were tested to determine their oil and water repellency, then subjected to a series of 15 washings by the home laundering method described above. After each third laundering operation, the tests for oil and water repellency were repeated. (To prevent interference of residual detergent with the water and oil repellency tests, the fabrics were rinsed with carbon tetrachloride each time prior to applying the said tests.) Also, after the 6th, 9th, 12th, and 15th laundering operations, the samples were measured in order to ascertain the area shrinkage. The results obtained are tabulated below:

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Run	Copolymer	Amount of Copolymer on fabric, %	Test	Number of home Launderings					
				0	3	6	9	12	15
1	Poly-PFOA/MAC 3/1	5.1	Oil repellency	130	70	70	0	0	0
			Water repellency	90	90	100	70	80	80
			Area shrinkage, %	—	—	0	0	0	3
2	do.	2.2	Oil repellency	130	60	60	50	0	0
			Water repellency	90	90	100	70	80	80
			Area shrinkage, %	—	—	1	2	5	10
3	do.	1.1	Oil repellency	130	50	60	0	0	0
			Water repellency	90	90	100	80	80	80
			Area shrinkage, %	—	—	2	4	11	16
4	Poly-PFOA/MAC 1/1	6.2	Oil repellency	130	60	90	50	50	0
			Water repellency	90	90	100	80	80	80
			Area shrinkage, %	—	—	1	2	4	9
5	do.	2.3	Oil repellency	130	50	70	50	0	0
			Water repellency	100	90	100	70	70	70
			Area shrinkage, %	—	—	1	3	5	20
6	do.	1.1	Oil repellency	130	50	70	50	0	0
			Water repellency	90	90	100	100	70	80
			Area shrinkage, %	—	—	1	5	9	20
7	Poly-PFOA/MAC 9/1	6.4	Oil repellency	130	70	100	90	60	60
8	Control (Untreated fabric)	0	Oil repellency	0	—	—	—	—	—
			Water repellency	60-70	—	—	—	—	—
			Area shrinkage, %	—	—	15	20	—	—

D: Further Tests on PFOA/MAC Treated Fabric
 Samples of the wool fabric treated with 5 PFOA/MAC copolymers by the procedure of Example I, Part B and a sample of the untreated fabric (control) were subjected to a series of mechanical tests to compare their properties. The results are tabulated below:

Test	Fabric treated with 2.8% poly-PFOA/MAC 1/1	Fabric treated with 2.8% poly-PFOA/MAC 3/1	Untreated fabric (control)
Flexural rigidity <i>a</i> (warp), mg-cm	159	186	100
Wrinkle recovery <i>b</i> (warp), degrees	148	147	148
Fabric break strength <i>c</i> (warp), lbs.	18.3	17.2	15.2
Fabric tear <i>d</i> (Elmendorf), gm	16	16	17
Abrasion resistance <i>e</i> , cycles	505	551	508

NOTES TO TABLE:

- a* Cantilever procedure ASTM D1388—55T
- b* ASTM D1295—53T, using the Monsanto wrinkle recovery tester
- c* ASTM D38—40, cut strip method, 6" x 1" samples, 3" gauge 20 sec. to break
- d* ASTM D1424—56T, using the Elmendorf falling pendulum tester
- e* Stoll abrader, ASTM D1175—55T

5 Samples of the wool fabrics treated with PFOA/MAC copolymers by the procedure of Example I, Part B, and a sample of the untreated fabric (control) were subjected to tests for acid, alkali, and peracetic solubility. These tests were performed as follows:

10 *Acid Solubility:* Samples were exposed 1 hour to 4 M HCl at 65°C. Loss in weight is measure of acid solubility.

Alkali Solubility: Samples were immersed 1 hour in 0.1 M NaOH at 65°C. Loss in weight is a measure of alkali solubility.

15 *Peracetic Acid Solubility:* Samples were exposed 25 hours to 2% peracetic acid, then treated with 0.3% ammonia. Loss in weight is a measure of solubility in this medium.

The results obtained are tabulated below:

Acid, Alkali, and Peracetic Solubility of PFOA/MAC-Treated Fabrics

Copolymer	Amount of copolymer on fabric, %	Solubility in		
		Acid, %	Alkali, %	Peracetic acid, %
Poly-PFOA/MAC (1/1)	6.1	7.8	4.5	82.7
do.	4.0	6.8	6.2	—
do.	2.6	8.4	7.6	83.6
Poly-PFOA/MAC (3/1)	6.4	6.9	5.5	81.1
do.	4.0	8.5	7.7	—
do.	2.0	8.1	7.5	82.3
None (control)	0	13.0	9.8	81.9

20 In order to test the resistance of the applied copolymers to solvents, samples of the wool fabrics treated with poly-PFOA/MAC were subjected to continuous extraction with benzotrifluoride in a Soxhlet ex-

tractor. At intervals, weighings were made to determine the amount of polymer remaining on the fabric.

25 The results are summarized below:

Copolymer	Hours of extraction				
	0	6	13	20	27
Poly-PFOA/MAC (1/1)	3.8	2.2	2.2	2.2	2.2
Poly-PFOA/MAC (3/1)	3.5	2.7	2.7	2.7	2.7

EXAMPLE II

The following solutions were prepared:

5 (a) An aqueous solution containing 2% hexamethylene diamine, 2% sodium carbonate, and 0.1% wetting agent ("Triton X-100", isoctylphenyl ether of polyethylene glycol).

(b) A solution in benzotrifluoride of 3% sebacoyl chloride and 5% of poly-PFOA/MAC 9/1 (prepared as described in Example 10 I, part A).

Samples of wool (7.06 oz. per sq. yd. undyed woolen flannel, 33 ends and 33 picks per inch) were treated with the above solutions in the following manner: The wool

15 was immersed in solution (a) for 30 seconds, removed, passed through squeeze rolls to provide a wet pick-up of 70%, immersed for 30 seconds in solution (b) removed, passed through the squeeze rolls again, and washed in warm water containing 2% acetic acid and 0.1% wetting agent ("Triton X-100" isoctylphenyl ether of polyethylene glycol). The samples were then rinsed and air dried. The amount of resin formed on the fabric was 2.8%.

20 25 The treated samples were tested as described in Example I, part C. The results are tabulated below:

Fabric tested	Test	Number of home launderings					
		0	3	6	9	12	15
Treated fabric	Oil repellency	110	60	90	80	50	70
	Water repellency	90	80	80	80	70	80
	Area shrinkage, %	—	—	0	0	1	1
Untreated fabric (control)	Oil repellency	0	—	—	—	—	—
	Water repellency	60—70	—	—	—	—	—
	Area shrinkage, %	—	—	15	20	—	—

30 EXAMPLE III

Abbreviations: In this example, ethyl acrylate-methacryloyl chloride copolymers are referred to as "poly-EA/MAC". Molar ratios are expressed as 1/1, 9/1, etc., as with the copolymers referred to above.

35 A mixture of ethyl acrylate (0.03 mole), methacryloyl chloride (0.01 mole), and 50 mg. α,α' - azodiisobutyronitrile was heated in a closed vessel for 3-1/2 hours at 78°C. 40 The product (poly-EA/MAC 3/1) was a hard, brittle resin.

45 The same monomers were reacted in the same manner as above but varying the proportions to produce two other copolymers, i.e., poly-EA/MAC 1/1 from equimolar proportions of ethyl acrylate and methacryloyl chloride and poly-EA/MAC 9/1 from 9 moles ethyl acrylate to one mole methacryloyl chloride.

50 Each of the EA/MAC copolymers described above was dissolved in a minimum quantity of ethyl acetate, then the solution

55 was diluted with the same solvent to the desired concentration. In this way, solutions at concentration levels of 10%, 7% and 4% were prepared from each of the copolymers. (The different concentration levels were provided to enable application of varying amounts of the copolymers onto a fabric). The solutions were applied to samples of wool fabric (7.05 oz. per sq. yd. undyed woolen flannel, 33 ends and 33 picks per inch) in the following manner: The fabric was immersed in the copolymer solution, then passed through squeeze rolls to provide a wet pick-up of about 70%. The treated fabric was then placed in an oven at 105°C for about 1-1/2 hours in order to cure the resin and bond it to the wool. After curing, the samples were weighed to determine the amount of copolymer on the fabric.

60 65 70 The treated samples were then treated for shrinkage by the Accelerotor method described above. The results are tabulated below:

Run	Copolymer	Amount of copolymer on fabric, %	Area shrinkage (Accelorotor method), %
1	EA/MAC 1/1	7.0	1
2	do.	4.7	4
3	do.	3.8	13
4	do.	2	14
5	EA/MAC 3/1	6.3	8
6	do.	4.3	10
7	do.	2.5	15
8	EA/MAC 9/1	6.5	18
9	do.	4.7	18
10	None (Untreated fabric)	0	25

5 In order to test the resistance of the applied copolymers to solvents, samples of the wool fabrics treated with poly-EA/MAC were subjected to continuous extraction with ethyl acetate in a Soxhlet extractor. At intervals,

weight measurements were made to determine the amount of copolymer remaining on the fabric. The results are summarized below:

10

Copolymer	Hours extracted			
	0	7	14	21
EA/MAC 1/1	6.2	4.5	4.3	4.2
EA/MAC 3/1	6.3	5.2	5.1	5.0

EXAMPLE IV

15 A mixture of 1,1,11 - trihydro - perfluoro-undecyl acrylate (6 g., 0.01 mole), methacryloyl chloride (0.33 g., 0.0033 mole), and 50 mg. of α,α' - azodisobutyronitrile was heated in a closed vessel at 78°C for 3-1/2 hours. The product was a waxy solid copolymer.

20 Samples of the copolymer were dissolved

in benzotrifluoride to prepare solutions containing 1.5%, 3%, and 6% of the copolymer. These solutions were applied to wool and the treated wool cured, in the manner as described in Example III. The products were then tested for shrinkage and water repellancy.

25 The results are tabulated below:

Run	Amount of copolymer on wool, %	Area shrinkage (Accelerator method), %	Water repellancy
1	1.5	15.4	70
2	3	10.7	80
3	6	4.9	80

EXAMPLE V

6 g. (0.025 mole) lauryl methacrylate
 2 g. (0.0044 mole) PFOA
 5 0.45 g. (0.0045 mole) MAC
 0.1 g. α, α' - azodiisobutyronitrile

The ingredients listed above were mixed

and heated in a closed vessel at 80°C for 3 hours. The resulting polymer was dissolved in ethyl acetate, to prepare solutions containing 0.5, 1.5, 3 and 6% of the polymer. These solutions were applied to wool and the treated wool cured, all as described in Example III. The results of various tests on the products are tabulated below:

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Run	Amount of polymer on wool, %	Area shrinkage (Accelerator method), %	Oil repellency	Water repellency
1	0.5	6.0	60	70
2	1.5	2.0	60	70
3	3.0	1.0	70	70
4	6.0	1.0	80	80

The words TIDE and TRITON used herein are Registered Trade Marks.

WHAT WE CLAIM IS:

1. A process of treating a hydrogen-donor textile material to improve its properties 20 which comprises reacting said textile material with a copolymer applied thereto as such or formed *in situ* on the textile material, said copolymer being a copolymer of (1) an acid chloride which is acryloyl chloride or methacryloyl chloride and (2) a different compound which is copolymerizable with said acid chloride, which contains at least one $\text{CH}_2=\text{C}<$ grouping and which is free from any hydrogen atom reactive with an acid 25 chloride grouping.

2. A process of treating a hydrogen-donor textile material to improve its properties which comprises impregnating such textile material with a copolymer of (1) an acid chloride which is acryloyl chloride or methacryloyl chloride and (2) a different compound which is copolymerizable with said acid chloride, which contains at least one $\text{CH}_2=\text{C}<$ grouping, and which is free from 30 any hydrogen atom reactive with an acid 35 chloride grouping.

3. The process of claim 2 wherein the compound of (2) is a fluoroalkyl acrylate or fluoroalkyl methacrylate.

4. The process of claim 2 wherein the compound of (2) is an ester of the formula—

$$\text{CF}_3-(\text{CF}_2)_n-\text{CH}_2-\text{O}-\overset{\text{O}}{\underset{\text{R}}{\text{C}}}=\text{CH}_2$$

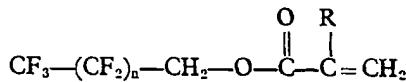
wherein R is H or CH_3 , and n is an integer from 0 to 18.

5. The process of claim 2 wherein the compound of (2) is 1,1-dihydroperfluoro-octyl acrylate.

6. A process for reducing the felting and shrinking tendencies of wool which comprises impregnating the wool with a solution, in an inert, volatile solvent, of a co- 45 50 55 60

5 polymer of (1) an acid chloride which is acryloyl chloride or methacryloyl chloride and (2) a fluoroalkyl acrylate or fluoroalkyl methacrylate, and heating the resulting impregnated wool to volatilize said solvent and to effect reaction between said wool and said copolymer thereby insolubilizing the latter *in situ* on the wool.

7. The process of claim 6 wherein the 10 ester of (2) has the formula—



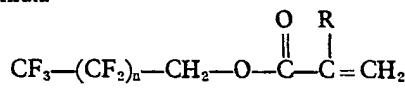
wherein R is H or CH₃, and n is an integer from 0 to 18.

8. The process of claim 6 wherein the 15 ester of (2) is 1,1 - dihydroperfluoroctyl acrylate.

9. Hydrogen-donor textile material impregnated and chemically bound with a copolymer of (1) an acid chloride which is 20 acryloyl chloride or methacryloyl chloride and (2) a different compound which is copolymerizable with said acid chloride, which contains at least one CH₂=C< grouping, and which is free from any hydrogen atom reactive with an acid chloride grouping.

10. The product of claim 9 wherein the 25 said compound of (2) is a fluoroalkyl acrylate or fluoroalkyl methacrylate.

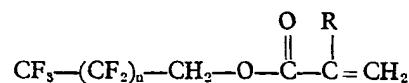
11. The product of claim 9 wherein the said compound of (2) is an ester of the 30 formula



wherein R is H or CH₃ and n is an integer from 0 to 18.

12. The product of claim 9 wherein the compound of (2) is 1,1 - dihydroperfluoroctyl acrylate.

13. The product of claim 9 wherein the textile material is wool and wherein the compound of (2) is a compound of the formula— 40



wherein R is H or CH₃ and n is an integer from 0 to 13.

14. The product of claim 9 wherein the textile material is wool and the copolymer is a copolymer of methacryloyl chloride and 45 1,1 - dihydroperfluoroctyl acrylate.

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